

New molecule-based catalyst to produce H₂ by metallo-porphine dispersed into polymer membrane

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Received 15 April 1998; accepted 9 June 1998

Abstract

Electrocatalytic proton reduction was studied with metallo-tetraphenylporphine (MTPP) incorporated into a Nafion membrane (Nf[MTPP]) coated on a basal-plane pyrolytic graphite (BPG) electrode or a Pt electrode. It was found that when M = Mn and Fe, Nf[MTPP] can work as a highly active catalyst to produce dihydrogen. Especially in a Pt base electrode system, it was shown that the electrocatalytic H⁺ reduction by the electrode-coated Nf[MTPP] takes place even at the theoretical H⁺/H₂ redox potential (−0.25 V vs. Ag/AgCl, at pH 1.0), and that its catalytic activity is much higher than that of a neat MTPP and a conventional Pt catalyst. When the catalysis of the Pt/Nf[MnTPP] system was investigated with respect to MnTPP concentration in the membrane ([MnTPP]_{Nf}), the amount of the dihydrogen produced decreased with the increase of [MnTPP]_{Nf}. The catalysis was discussed in terms of the electron transfer process to generate the electroactive species for H₂ production as well as the characteristics around the catalyst site in the membrane. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Metalloporphyrin; Proton reduction; Dihydrogen production; Molecular catalyst; Photosynthetic model

1. Introduction

Proton reduction to produce H₂ is not only a fundamental redox reaction but also an important research subject in the field of energy conversion. Water photolysis to obtain dihydrogen and dioxygen is a promising model in constructing an artificial photosynthetic system, but the system composed of molecule-based system is not established. As a strategy to this goal, it is

of importance that highly active molecular catalysts are developed to produce O₂ and H₂ at oxidation/reduction sites. In the reduction site to produce H₂, it has been known that platinum colloids work as the most active catalysts [1–3]. However, it is a problem that the catalytic activity of metal catalysts often changes with their preparation method. This arises from the changes of the particle size and effective area of the catalyst sites. It is of importance to establish molecule-based oxidation/reduction catalysts to design an efficient and stable energy resource. However, there has been almost no molecule-based catalyst for H⁺ reduction.

We have been studying heterogeneous catalyst systems composed of a metal complex and

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a polymer film for water oxidation and CO_2/H^+ reduction [4–13]. Such a molecule-based system is a promising candidate to construct a photochemical energy conversion system because the reaction components can be arranged in a molecular level in the matrix. It can also be expected that a molecule-based catalyst system results in some specific catalysis such as cooperative interaction between the catalysts, concentration effect of the substrates into a matrix, etc.

In the present work, we have found that when $\text{M} = \text{Mn}$ and Fe , metallo-tetraphenylporphyrins (MTPP, $\text{M}: \text{Mn}, \text{Fe}$) dispersed into a Nafion[®] (Nf) membrane coated on a basal-plane pyrolytic graphite (BPG) electrode (BPG/Nf[MTPP]) are active electrocatalysts to reduce protons. In such a catalyst system, it should be noted that the electron transfer process to generate electroactive species is an important factor in the overall catalysis. The electron transfer process was studied by an in situ potential-step chronoamperometry (PSCAS) to understand the present electrocatalysis, and the result will be discussed.

2. Experimental

2.1. Material and preparation of modified electrode

Both MTPP and a 5 wt.% Nf alcoholic solution were purchased from Aldrich Chemical. A dimethylformamide (DMF) solution containing 0.2 mM MTPP and 0.5 wt.% Nf was prepared prior to the electrode preparation. The preparation of the modified electrode was carried out by casting the mixture solution (10 μl or 50 μl) onto a BPG (effective area, 0.21 cm^2) or a Pt electrode (effective area, 1 cm^2) followed by solvent evaporation under vacuum. An indium–tin oxide electrode (ITO, effective area; 1 cm^2) was modified the same as the modified Pt. The membrane thickness of Nf was estimated to be ca. 1.2 μm .

2.2. Electrochemical study

A single compartment cell was equipped with a Nf[MTPP] coated working, a spiral platinum wire counter and a silver/silver chloride (Ag/AgCl, in saturated KCl electrolyte) reference electrode. The electrochemical study was carried out by the use of a potentiostat (Hokuto Denko, HA-301) equipped with a function generator (Hokuto Denko, HB-104), a coulomb meter (Hokuto Denko, HF-201) and an X–Y recorder (Rika Denki, RW-211). In situ potential-step chronoamperometry (PSCAS) was carried out in combination of the voltammetric apparatus with a spectrophotometer (Otsuka Denshi, IMUC-7000) equipped with a photodiode array detector. All of the electrochemical measurements were run in a pH 1.0 aqueous phosphate buffer solution. The hydrogen produced in the electrolysis was analyzed by a gas chromatograph (Shimadzu, GC-4CPT) with a molecular sieve 5 Å column and argon carrier gas.

3. Result and discussion

Fig. 1 shows the cyclic voltammogram (CV) at Nf[MnTPP]-coated ITO electrode in a pH 1.0 aqueous solution. The redox potential of $\text{Mn}^{\text{III/II}}$ is shown at -0.12 V (vs. Ag/AgCl) (the mid-

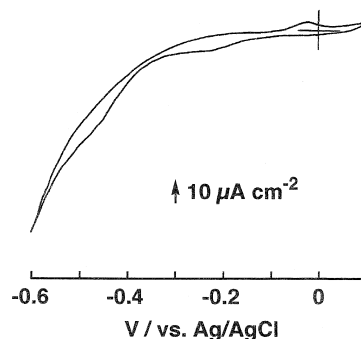


Fig. 1. Results of CV measurement at ITO electrode coated with Nf[MnTPP] at pH 1.0 under Ar. The total amount of MnTPP coated on the electrode surface was 1.0×10^{-8} mol cm^{-2} . Scan rate, 10 mV s^{-1} .

point potential between the anodic and cathodic peaks). In the more reductive scan, a cathodic shoulder peak appeared around -0.48 V. When a similar CV measurement was carried out with a bare ITO electrode, a shoulder peak was also observed at -0.48 V showing that the reduction of ITO itself takes place at that potential.

Fig. 2 shows CVs at both a Pt/Nf[MnTPP] and a bare Pt in a pH 1.0 aqueous solution. The cathodic current due to proton reduction starts to increase in more positive potential regions at the Pt/Nf[MnTPP] than at a bare Pt. In a separate experiment, a similar measurement was carried out at a Pt/Nf[FeTPP]. The electrochemical behavior of a Pt/Nf[FeTPP] was almost the same as that of a Pt/Nf[MnTPP] in this potential region. Although Pt itself is active to reduce H^+ , the modification of the electrode surface by MTPP-dispersed Nafion membrane results in more efficient catalyst system for the H^+ reduction.

Potentiostatic electrolysis was carried out at the Pt/Nf[MTPP] compared with a neat MnTPP (Pt/MTPP), a Nf-coated Pt (Pt/Nf) and a bare Pt. The typical results are shown in Table 1. It was found that much higher amount of H_2 was

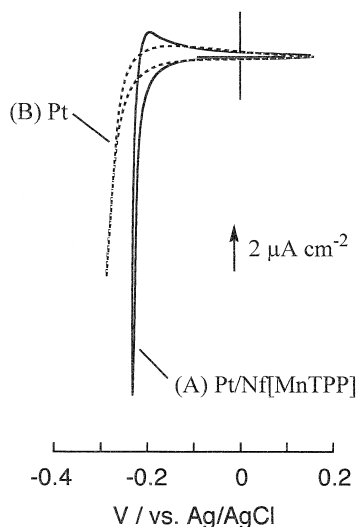


Fig. 2. Cyclic voltammogram at Pt electrode coated with Nf[MnTPP] (A) and Pt bare electrode (B) in a phosphate buffer solution (pH 1.0) under Ar. Scan rate, 1 mV s^{-1} .

Table 1
Results of potentiostatic electrolysis (1 h) by using modified Pt electrode in a 1.0 aqueous solution

System	H_2 produced/ μl	
	Potential/V vs. Ag/AgCl	
	-0.25	-0.30
a bare Pt	2.15	14.4
Pt/Nf	2.83	34.6
Pt/FeTPP ^a	2.55	5.31
Pt/Nf[FeTPP] ^a	2.68	208
Pt/MnTPP ^a	1.30	17.9
Pt/Nf[MnTPP] ^a	4.12	68.1

^aThe coated amount of MTPP was $1.0 \times 10^{-8} \text{ mol cm}^{-2}$.

produced in the Pt/Nf[MTPP] system than in other ones. It should be noted that the catalytic activity of Pt/Nf[MTPP] to reduce H^+ exceeds that of a bare Pt. In a pH 1 aqueous solution, theoretical potential of H^+/H_2 is -0.25 V (vs. Ag/AgCl). Therefore, it is noted that Nf[MTPP] can work as a new molecular catalyst to reduce protons with almost no overpotentials.

The same electrolysis study was carried out using a BPG electrode instead of a Pt electrode. The typical results are shown in Table 2. It was again found that BPG/Nf[MTPP] can produce much higher amount of H_2 than other systems such as a neat MTPP (BPG/MTPP), Nf-coated BPG (BPG/Nf) and a bare BPG. The turnover number (TN) of the MTPP to produce H_2 was about 500 h^{-1} . In a BPG base electrode system the electrocatalytic H^+ reduction by Nf[MTPP] took place in more negative potential regions than a Pt base electrode system. This is ascribed to the difference of the electroconductivity between the Pt and BPG electrodes.

Table 2
Results of potentiostatic electrolysis (1 h) at -0.8 V (vs. Ag/AgCl) by using modified BPG electrode in a pH aqueous solution

System	H_2 produced/ μl			
	BPG/Nf[MTPP] ^a	BPG/MTPP ^a	BPG/Nf	a bare BPG
MnTPP	23.6	0.54	1.19	0.34
FeTPP	34.7	2.50	0.69	0.09

^aThe coated amount of MTPP was $1.0 \times 10^{-8} \text{ mol cm}^{-2}$.

From the electrolysis data in a Pt base or a BPG base electrode system, it was found that much more efficient catalysis by the MTPPs takes place by dispersion into a Nf membrane. Choi et al. [14] have reported that the potential at which Fe(III)TPP is reduced to Fe(II)TPP (-0.29 V vs. SCE) is similar to that of Mn(III/II)TPP. Therefore, the catalyst is reduced by only one electron in the applied potential region. Since H_2 production is a 2-electron process, bimolecular catalysis by the one-electron reduced MTPP should take place to reduce protons to H_2 . It is most probable that such a specific bimolecular catalysis is induced efficiently by using such a heterogeneous reaction system. It is also to be noted that the amount of H_2 produced at the Nf-coated electrode is higher than that of a bare electrode. This is ascribable to the high acidity of the sulfonate groups on the Nf side chain. The local pH in the Nf membrane must be much lower than that of a bulk electrolyte solution, so that the Nf works as a proton sources for the catalysis on the base electrode.

In order to understand the catalytic features of the Nf[MTPP], the potentiostatic electrolysis was carried out as a function of the MnTPP concentration in the Nf membrane ($[MnTPP]_{Nf}$) at the applied potential of -0.3 V. The relationship of the amount of H_2 produced versus $[MnTPP]_{Nf}$ is shown in Fig. 3; this was carried out with a constant thickness of the membrane. Though the total amount of the MnTPP increases with $[MnTPP]_{Nf}$, the amount of H_2 produced decreased with the concentration. The overall kinetics in the electrocatalytic H_2 production might be controlled by some other factors, especially in higher $[MnTPP]_{Nf}$.

The present authors have reported recently that a heterogeneous electrocatalysis is associated with the electron transfer process taking place by hopping [12,13] or physical diffusion [15] to generate electroactive species. An in situ PSCAS was carried out to understand the electron transfer process of the present system. Typical spectrum changes after potential step from

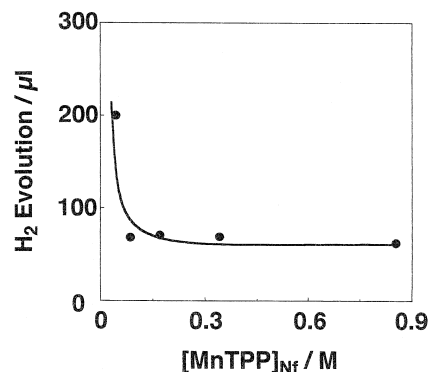


Fig. 3. The relationship between the amount of H_2 produced and the MnTPP concentration in Nf membrane ($[MnTPP]_{Nf}$) on a Pt electrode for the potentiostatic electrolysis (1 h) at -0.30 V (vs. Ag/AgCl) in a pH 1.0 aqueous solution under Ar.

0 V to -0.30 V (vs. Ag/AgCl) are shown in Fig. 4. The absorption band of the Mn(III) TPP at 475 nm decreased, and a new band at 430 nm appeared due to the formation of Mn(II)TPP. Similar PSCAS measurements were carried out with various $[MnTPP]_{Nf}$ (from 0.043 M to 0.85 M), and the electroactive ratio (R_{et}) of Mn(III)TPP was estimated by the following equation,

$$R_{et} = (A_0 - A_t) / [(\epsilon_{III} - \epsilon_{II}) \times c \times l]$$

where A_0 and A_t are the absorbance at the initial and t seconds, respectively. Both ϵ_{III} and ϵ_{II} are the molar absorption coefficients of the Mn(III)TPP and Mn(II)TPP in the Nf membrane, c the total concentration of MnTPP in the Nf membrane, and l the thickness of Nf on the electrode surface. The relationship of the electroactive amount of Mn(III)TPP (\bullet) (nmol) and the R_{et} (\square) (fraction) with respect to the $[MnTPP]_{Nf}$ is shown in Fig. 5. It was found that the amount of the electrogenerated Mn(II)TPP increased with $[MnTPP]_{Nf}$, and that the R_{et} decreased with increasing $[MnTPP]_{Nf}$. If the electron transfer occurs by a hopping process between the redox centers, it is a bimolecular process and the R_{et} should increase with $[MnTPP]_{Nf}$. However, the results of Fig. 5 show that the electron transfer takes place by a monomolecular process called physical diffu-

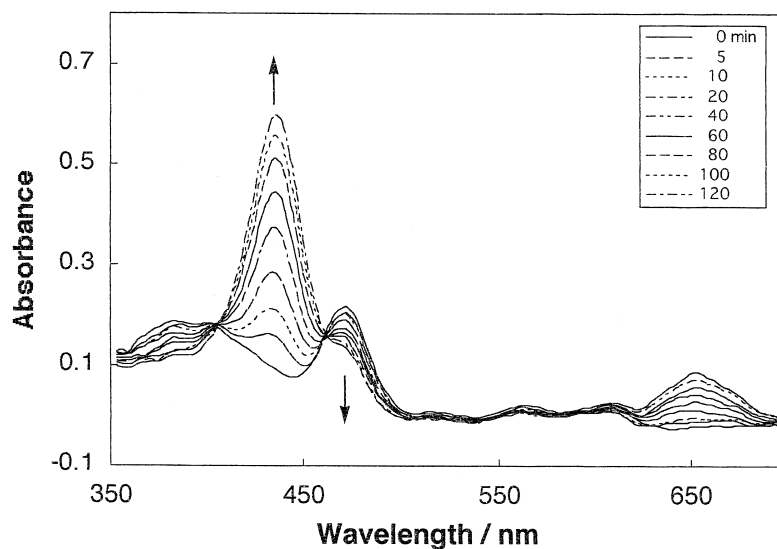


Fig. 4. Visible absorption spectral change of 0.34 M Mn(III)TPP to Mn(II)TPP in the Nf membrane with the sample time after the potential step from 0 to -0.3 V (vs. Ag/AgCl).

sion. The net TN of the MnTPP for proton reduction is obtained based on the electroactive amounts of the complex, and the plot of net TN vs. $[\text{MnTPP}]_{\text{Nf}}$ is shown in Fig. 6. The net TN decreased with increasing $[\text{MnTPP}]_{\text{Nf}}$. Since the tendency of the R_{et} is much different from that of the TN, it is most likely that the overall kinetics to catalyze proton reduction would not be controlled by the electron transfer process.

The electrocatalytic H^+ reduction to produce H_2 must take place by a bimolecular catalysis of a 1-electron reduced MTPP as described

before. As for the intermediate, there are following possibilities; (1) metal–hydride, and (2) π –proton complex of the phenyl group. It has been reported that the cation– π interaction is responsible for the ion selectivity in potassium channels of biological systems [16,17]. It is inferred that the hydrophobic MTPP complex is present in a hydrophobic region or an interfacial region between hydrophilic and hydrophobic columns in the Nf membrane [18], and such a hydrophobic microenvironment might favor the π – H^+ intermediate rather than the M–H hydride one.

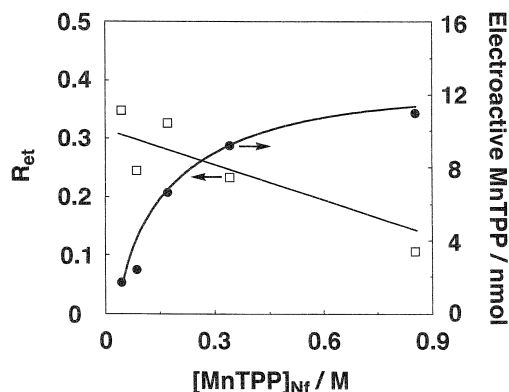


Fig. 5. R_{et} (□) and electroactive MnTPP (●) against MnTPP concentration in Nf membrane ($[\text{MnTPP}]_{\text{Nf}}$).

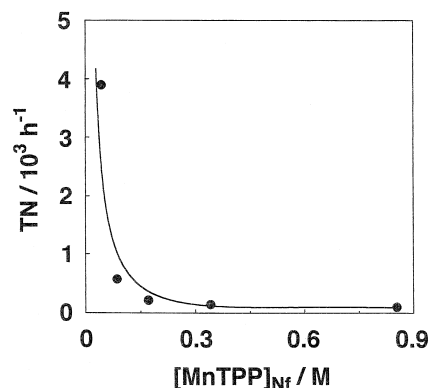


Fig. 6. The relationship between TN and MnTPP concentration in Nf membrane ($[\text{MnTPP}]_{\text{Nf}}$).

In the present system, the most characteristic feature is that the amount of the H_2 produced decreases with increasing $[MnTPP]_{Nf}$. However, since the results of the electron transfer analysis showed that the amount of electrogenerated Mn(II)TPP increased with $[MnTPP]_{Nf}$, the catalysis of the Nf[MTPP] could not be associated directly with the electron transfer process. Therefore, it is considered that the H_2 formation from the intermediates will be a rate-determining step. MTPP itself is a hydrophobic molecule, so that the property of the Nf must become more hydrophobic with increasing $[MnTPP]_{Nf}$. An intermediate complex (MTPP $\cdots H^+ \cdots H^+ \cdots$ MTPP) would be formed before H^+ reduction. However, such a complex formation with polar nature would be unfavorable in a hydrophobic environment. Therefore, hydrogen production would be suppressed in higher $[MnTPP]_{Nf}$.

In conclusion, it was found that MTPP dispersed into a Nf membrane can work as a molecular catalyst to reduce protons with high activity. It is noteworthy that the Nf[MTPP] coated on a Pt electrode results in hydrogen production even at the theoretical potential of H^+/H_2 .

Acknowledgements

The authors acknowledge the Grant-in-Aid for Scientific Research Priority Area of 'New polymers and Their Nano-Organized Systems'

(No. 277/09235202) from Ministry of Education, Science, Sports and Culture. T.A. has been granted the JSPS Research Fellowships for Young Scientists.

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